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***Abstract*—The picosecond relaxation of an electronically excited insulator is described by means of an extension of the two-temperature model. In this phenomenological description, charge neutrality is enforced, but the electron and hole chemical potentials are not forced to be equal. Different experimental regimes can be characterized by comparing the electron-lattice and electron-hole relaxation rates. The dependency of the long-time relaxation on both the electronic gap and the sample density is discussed. The extend two-temperature model correctly describes the unexpectedly long transient opacity displayed by a borosilicate glass irradiated by ultrafast proton pulses.**

Keywords–Proton irradiation; Insulators; Electron-hole plasma; Two-temperature model.

I. Introduction

By means of the target normal sheath acceleration mechanism, ultrafast (3 ± 0.8 ps) proton pulses with a very sharp energy (15 ± 1.5) MeV can be generated at local-scale laser facilities, like the TARANIS multi-terawatt laser at Queen's University Belfast [1]. This novel experimental capabilities are ideally suited to investigate the relaxation of the electron-hole plasma generated upon proton irradiation of solids and liquids. For instance, the transient opacity of transparent insulators [2][3] and water [4] over a few hundreds of ps after the proton passage can be monitored using optical streaking. These early experiments have revealed an unexpectedly long (>100 ps) transient opacity in the near infrared (1054 nm probe). This unexpected behavior has been linked to the persistence of a 'cold' electron-hole plasma which causes the extinction of the probe.

In this paper, we introduce a simple extension of the Two-Temperature Model (TTM) [5] which describes the experimental results using two phenomenological time-scales. The first time-scale is related to the well-known electron-lattice (or electron-phonon) relaxation [6], while the second time-scale is related to the relaxation of the electrons and holes to a common 'chemical' equilibrium. In particular, we find that the transient opacity of an irradiated borosilicate (BK7) glass is well described by a short electron-phonon time-scale (<10 ps) — in agreement with previous estimates — and a longer 'chemical' relaxation time-scale of 110 ps. A microscopic justification of the longer 'chemical' relaxation of the electron-hole plasma using an excitonic relaxation model [7][8] is currently attempted.

This paper is organized as follows: Section II describes the phenomenological kinetic equations used to model the experiments; Section III contains the main results of the paper; Finally, Section IV provides a brief discussion of the underlying microscopic mechanisms and a proposal for the validation of the model.

II. Kinetic model

In order to model the electron-hole plasma generated upon proton irradiation, we made the following assumptions: i) The plasma is classical and Boltzmann statistics applies; ii) The plasma is well described by a gas of non-interacting particles (ideal gas); iii) The plasma is homogeneous, *i.e.*, the electron and hole concentrations do not depend on the position, $\boldsymbol{r}$; iv) The electrons and holes have equilibrated separately, although a global equilibrium has not reached yet.

The first assumption is not crucial and will be relaxed (see Section III). The Boltzmann statistics is used here to keep the presentation simple and uncluttered. The second assumption is strictly justified at low concentration, but no attempt to include the may-body interaction is described in this paper. The third and fourth assumptions are valid after 10–100 fs, *i.e.*, the time it takes to the electrons and holes to diffuse about the proton track and equilibrate through fast collisional processes. These final assumptions can be independently validated by solving a set of coupled charge and energy transport equations [7] based on a convenient hydrodynamic approximation [9].

To model the long (>100 ps) relaxation dynamics probed by the experiments of Dromey *et al.* [2][3][4], the full solution of the coupled charge and energy transport equations, *e.g.*, using finite element models, still requires a considerable numerical effort. Those are equations for the electrostatic potential, $\phi(\boldsymbol{r}, t)$, the electron and hole concentrations, $n(\boldsymbol{r}, t)$ and $p(\boldsymbol{r}, t)$, the electron and hole temperatures, $T_n(\boldsymbol{r}, t)$ and $T_p(\boldsymbol{r}, t)$, and the lattice temperature, $T_l(\boldsymbol{r}, t)$. In view of our assumption iii), we can immediately set $\phi = 0$ and neglect the dependence on $\boldsymbol{r}$. Assumptions iv) implies that we

can use the equilibrium expression for the electron and hole concentrations,

$$n(t) = \left(\frac{2}{\Lambda_e^3}\right) \exp\left(\frac{\mu_e}{k_B T_e}\right) \tag{1}$$

and

$$p(t) = \left(\frac{2}{\Lambda_p^3}\right) \exp\left(-\frac{E_g - \mu_p}{k_B T_p}\right) , \tag{2}$$

where k_B is the Boltzmann constant, Λ_e and Λ_p are the thermal wavelengths of the electrons and holes [10], μ_e and μ_p are the chemical potentials of the electrons and holes, and E_g is the band gap. Energies are measured from the bottom of the conduction band.

Global charge neutrality requires that $n(t) = p(t)$. By further assuming that $T_e = T_p$, it can be shown that $\mu_e = \bar{\mu} + \xi/2$ and $\mu_h = -\bar{\mu} + \xi/2$, where $\bar{\mu} = -(E_g/2) + (3k_BT/4)\ln(m_h/m_e)$ is the average chemical potential, and we will refer to $\xi = \mu_e + \mu_p$ as the chemical bias. At 'chemical' equilibrium between particle at holes, we have that $\mu_p = -\mu_e$ or $\xi = 0$. We conclude the paragraph by rephrasing assumption iv) as: The electron and holes are in thermal equilibrium with $T_e = T_p$, but not yet in 'chemical equilibrium ($\xi > 0$).

As the electron-hole plasma evolves towards its 'chemical' equilibrium, the chemical bias, ξ, will decrease to zero. Concurrently, the plasma will evolves towards its thermal equilibrium with the lattice, reached when $T_e = T_l$. In view of this simple kinetic picture, we can write down the following coupled phenomenological equations:

$$\begin{cases} \left(\dfrac{\partial u}{\partial T_e}\right)_n \dot{T}_e = -\left(gn + \dfrac{1}{\tau_b}\left(\dfrac{\partial u}{\partial T_e}\right)_n\right)(T_e - T_l) \ , \\ \left(\dfrac{\partial u}{\partial \xi}\right)_n \dot{\xi} = -gn\,(T_e - T_l) - \dfrac{1}{\tau_b}\left(\dfrac{\partial u}{\partial \xi}\right)_n \xi \ , \end{cases} \tag{3}$$

where g, and τ_b are model parameters, u is the energy density of the electron-hole plasma, and $(\partial x/\partial y)_n$ stands for the derivative of x with respect to y taken at fixed electron concentration.

First of all, the equilibrium solution $T_e = T_l$ and $\xi = 0$ is a stationary solution of Eq. (3). Secondly, in the limit of $\tau_b \to \infty$, the equations reduce to $(\partial u/\partial T_e)_n \dot{T}_e = -gn\,(T_e - T_l)$, *i.e.*, a simple convective heat transfer equation between the electron-hole plasma and the lattice [5].

To clarify the $\tau_b \to \infty$ limit, we substitute Eq. (3) into the time-derivative of the electron concentration and obtain that

$$\dot{n} = -\frac{1}{\tau_b}\left[\left(\frac{\partial n}{\partial T}\right)_\xi (T_e - T_l) + \left(\frac{\partial n}{\partial \xi}\right)_T \xi\right] \tag{4}$$

Hence, the electron concentration gets fixed when $\tau_b \to \infty$. As a consequence, the second line of Eq. (3) becomes redundant in the limit of $\tau_b \to \infty$. Also note that the last line of Eq. (4) represents a pseudo-first order 'chemical' kinetic with 'reaction' rate $1/\tau_b$. This 'chemical reaction' involves the non-radiative recombination of the electrons and holes.

The parameter, g, is related to the electron-phonon relaxation. It is worth noting that at the end of the proton irradiation experiment described in Refs. [2][3][4], the sample's macroscopic optical properties are completely recovered. As a consequence, a relatively small amount of energy is initially absorbed by the electron-hole plasma and eventually transferred to the lattice.

The time-derivative of the energy density of the electron-hole plasma is given by

$$\begin{aligned} \dot{u} &= -gn\,(T_e - T_l) \\ &-\frac{1}{\tau_b}\left[\left(\frac{\partial u}{\partial T_e}\right)_\xi (T_e - T_l) + \left(\frac{\partial u}{\partial \xi}\right)_T \xi\right] \end{aligned} \tag{5}$$

where in the first step we have used Eq. (4). By equating the energy lost by the electron-hole plasma to the energy gained by the lattice, we find the following equation for T_l,

$$\begin{aligned} 3\rho_l N_A k_B \dot{T}_l &= gn\,(T_e - T_l) \\ &+\frac{1}{\tau_b}\left[\left(\frac{\partial u}{\partial T_e}\right)_\xi (T_e - T_l) + \left(\frac{\partial u}{\partial \xi}\right)_{T_e} \xi\right] \ , \end{aligned} \tag{6}$$

where ρ_l is the molar density of the lattice and N_A is the Avogadro number.

In the limit of $\tau_b \to \infty$, the combined Eq. (3) and Eq. (6) give the well-known homogeneous TTM defined by

$$\begin{cases} \left(\dfrac{\partial u}{\partial T_e}\right)_n \dot{T}_e = -g'\,(T_e - T_l) \ , \\ 3\rho_l N_A k_B \dot{T}_l = g'\,(T_e - T_l) \ , \end{cases} \tag{7}$$

where $g' = gn$. Note that Eq. (7) has been used for modeling energy relaxation in metals [5], in which the electron concentration, n, is indeed fixed. We can then conclude that Eq. (3) along with Eq. (6) provide a simple phenomenological extension of the homogeneous TTM to the case in which the electron concentration is not fixed.

We end the section by mentioning that Eq. (3) satisfies the Onsager's reciprocal relations [10] and that all the equilibrium properties of our electron-hole plasma model can be obtained from grand potential density

$$\Omega(T_e, \xi) = -\left(\frac{4k_B T_e}{\Lambda_e^3}\right) \exp\left(\frac{\bar{\mu}}{k_B T_e} + \frac{\xi}{2k_B T_e}\right) , \tag{8}$$

or its straightforward extension to the degenerate case. For instance, we have that (see Eq. (1))

$$n = p = -\left(\partial\Omega/\partial\xi\right)_{T_e} \tag{9}$$

III. Results

In the experiments of Dromey *et al.* [2][3][4], the transient opacity of a transparent insulator is probed upon ultrafast proton irradiation. A 1053 nm infrared source is used as a probe. To interpret this kind of experiments, we assumed that the extinction is due to free carrier (electrons and holes) and we use a Drude model,

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} , \tag{10}$$

of the dielectric permittivity of the electron-hole plasma. In Eq. (10), ϵ_∞ is the dielectric permittivity of the transparent insulator (host material), $\omega_p = \sqrt{e^2 n/\epsilon_0 \bar{m}}$ is the plasmon frequency, with $1/\bar{m} = (1/m_e) + (1/m_p)$ being the reduced electron-hole mass, and γ is a phenomenological relaxation rate. The density, n, appearing in the plasmon frequency is obtained from Eq. (1) upon integration of the coupled

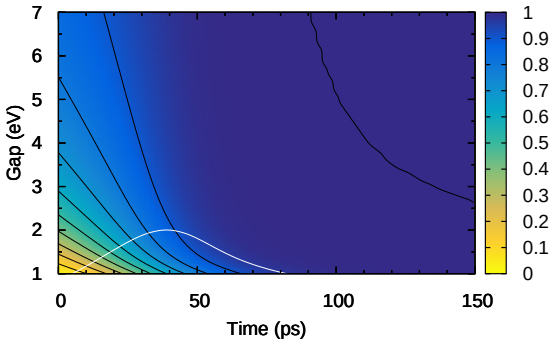

Figure 1. Map of the transmittance as function of the band gap and time, at fixed molar density. The the band gap of BK7 glass is approximately 3.5 eV, see text for the fixed model parameters. In the the region below the white line the electron-hole plasma is degenerate.

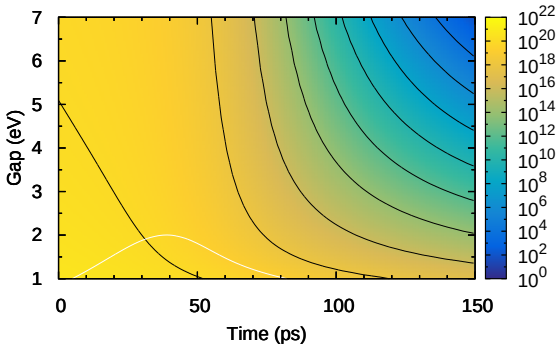

Figure 2. Map of the electron-hole pair density as function of the band gap and time, at fixed molar density. The the band gap of BK7 glass is approximately 3.5 eV, see text for the fixed model parameters. In the the region below the white line the electron-hole plasma is degenerate.

phenomenological equations, Eqs. (3) and (6). The results presented in this section are obtained using Fermi-Dirac statistics, although Boltzmann statistics gives a good approximation for most of the parameter values.

Following the experiments [2], we assume an average track density, of 50 tracks per $\mu\mathrm{m}^2$. Defining an effective track radius, R, the track polarizability is found as

$$\alpha(\omega) = 2\epsilon_0 \left(\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon(\omega) + \epsilon_\infty} \right) \pi R^2 \tag{11}$$

Finally, the extinction cross-section (dimensionally, it is a length, not an area) of the a track is

$$\sigma_{ext}(\omega) = \frac{k}{\epsilon_0} \mathrm{Im}\{\alpha(\omega)\} + \frac{k^4 |\alpha(\omega)|^2}{6\pi\epsilon_0^2}, \tag{12}$$

where the first term accounts for the absorption and the second one for the scattering [11]. The wave number is $k = \omega\sqrt{\epsilon_\infty}/c$, where c is the speed of light.

To fit the observed transient opacity of BK7 glass, we set the band gap, $E_g = 3.5$ eV, the sample molar density $\rho_l = 0.04$ mol/cm^3, and the refraction index, $\sqrt{\epsilon}_\infty = 1.5$. As an initial guess, we also set $m_p = m_e = 0.5$ mass of the electron. The stopping power of 15 MeV protons close to the Bragg peak is approximately $S_e = 12$ eV/Å [12]. The initial electron concentration is then set to $n_0 = \left(S_e/\pi R^2\right)/3E_g$ and the initial temperature to $T_0 = 2E_g/3k_B$ [7]. The initial condition fro the chemical bias, ξ_0, is found by solving $n_0 = n(T_0, \xi_0)$ (see Eq. (1)). Finally, we set the effective track radius as $R = 5$ nm. Given these physical parameters, a good fit of the experimental data is compatible with the following values of the free parameters: $\gamma = 17$ meV, $g = 2.5 \cdot 10^{-12}$ W/K, and $\tau_b = 110$ ps.

To get some insight into the qualitative behavior our model, we perform a 'sensitivity analysis' varying two physical parameters, E_g and ρ_l, while keeping fixed all the remaining parameters, including γ, g, and τ_b.

Figure 1 shows a map of the time-dependent transmittance as a function of the band gap. As a general trend, the transient opacity gets more pronounced and longer lived as the band gap decreases. For instance, amorphous silica, having a band gap

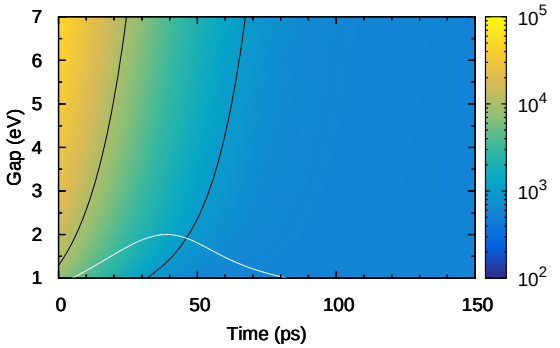

Figure 3. Map of the electronic temperature as function of the band gap and time, at fixed molar density. The the band gap of BK7 glass is approximately 3.5 eV, see text for the fixed model parameters. In the the region below the white line the electron-hole plasma is degenerate.

of about 9 eV and a molar density similar to that of the BK7 glass, is predicted to display a negligible transient opacity in an analogous proton irradiation experiment.

The trend with transmittance is well matched by the trend with electron-holes pair density, as shown in Figure 2. The match directly follows from our hypothesis that the transient opacity is due a sizable free carrier (electrons and holes) extinction upon proton irradiation.

The longer lived transient opacity is anti-correlated with the peak electronic temperature, as shown in Figure 3. This anti-correlation is a consequence of the competition between two relaxation mechanisms: 1) Thermal relaxation between the electron-hole plasma and the lattice; 2) 'Chemical' relaxation between electrons and holes. According to our model, the thermal relaxation mechanism is slower than the 'chemical' one for wide gap insulators, while the opposite is true for smaller gap insulators. In particular, the long lived transient opacity can be ascribed to persistent 'cold' (*i.e.*, in thermal equilibrium with the lattice) electron-hole plasma.

Finally, Figure 4 shows a map of the time-dependent transmittance as a function of the molar density. In this case, the transient opacity gets more pronounced and longer lived

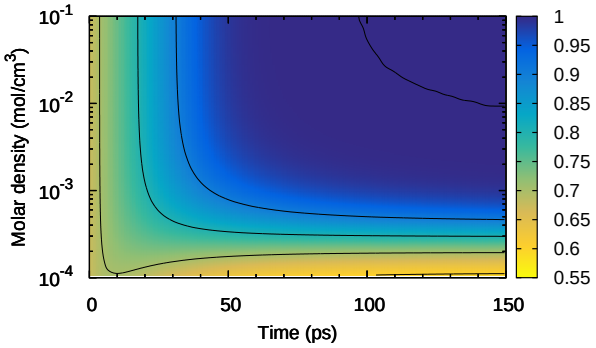

Figure 4. Map of the transmittance as function of the molar density and time, at fixed band gap. The molar density of BK7 glass is approximately $0.04\ \mathrm{mol/cm^3}$, see text for the fixed model parameters.

as the molar density decreases. Given the linear dependency of the heat capacity of the lattice on the molar density (see Eq. (6)), the thermal equilibrium between the electron-plasma and the lattice is quickly reached at a larger electronic temperature, T_e. As a consequence, the electron concentration is also larger and the electron-hole plasma extinction enhanced. Heat diffusion across the lattice will eventually cause the hot proton track to equilibrate to the temperature of the surrounding host material, namely room temperature. The competition between the thermal relaxation mechanism and the thermal diffusion is not considered in this paper.

IV. Discussion and conclusions

The phenomenological equations Eq. (3) and Eq. (6) provide a simple extension of the TTM to the case in which the electron concentration is not fixed. They can be readily generalized to include inhomogeneous electron and lattice temperatures, as in the inelastic thermal spike model [6]. Our proposal is complementary to the work of Daraszewicz and Duffy [13], who have extended the TTM by including an equation of motion for the electron concentration, n. In our proposal, n is a function of the electronic temperature, T_e, and the chemical bias, ξ. In particular, n is thermodynamically conjugated to ξ (see Eq. (9)). Using ξ is convenient because the 'chemical' equilibrium condition between electrons and holes, $\xi = 0$, is easily stated and enforced into the phenomenological equations.

From the fit of the experimental results, we obtain reasonable values of the free parameters γ and g. For a metal like iron, $n \approx 1.7 \cdot 10^{23}\ \mathrm{cm^{-3}}$, which gives $g' = gn \approx 4.3 \cdot 10^{11}\ \mathrm{W/cm^3 \cdot K}$, which compares favorably with the values found in literature [14]. On the other hand, the free parameter τ_b is inherent to our model and needs some microscopic justification. Starting from the early suggestion that an electron-hole plasma primarily decay into excitons [7], we assume that a 'chemical' equilibrium between the electron-hole plasma and the free excitons is rapidly reached. Hence, the rate-determining mechanism can be the slower (*i.e.*, activated) decay of the free excitons into self-trapped excitons [8]. The validation of this mechanism, along with other microscopic assumptions of the model, is currently attempted based on the full solution of the coupled charge and energy transport equations.

Acknowledgments

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